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Overview paper

ENVIRONMENTAL ASPECTS OF STRATOSPHERIC OZONE DEPLETION

Prepared by

Dr. B. W. BOVILLE
UNEP Consultant

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Table of Contents

1. Introduction
2. The Problem
3. The Natural Stratosphere and Ozone Layer
   - 3.1 The Stratosphere
   - 3.2 The Ozone Layer
4. Ozone and Related Measurements
5. Photochemistry and Minor Constituents
   - 5.1 The Role of Minor Constituents
   - 5.2 The Hydrogen System
   - 5.3 The Nitrogen System
     - 5.3.1 Fertilizers
     - 5.3.2 Aircraft
     - 5.3.3 Nuclear Explosions
     - 5.3.4 Galactic Cosmic Rays and Solar Proton Events
   - 5.4 The Chlorine System
6. Impact on Climate and Weather
7. Impact of Increased Ultraviolet Radiation
   - 7.1 The UV Spectrum
   - 7.2 The Photobiology of UV damage
   - 7.3 The Impact on Man
   - 7.4 The Impact on Plants
   - 7.5 The Impact on Terrestrial Animals
   - 7.6 The Impact on Ecosystems
   - 7.7 The Reduction of Harmful Effects
   - 7.8 Summary
8. Summary of Findings on Ozone Depletion and its Impact on Man and the Biosphere
9. Socio-Economic Aspects
   - 9.1 Introduction
   - 9.2 The Nitrogen System
   - 9.3 The Chlorine System
   - 9.4 Future Needs

1. Introduction

The Governing Council of UNEP at its meeting in April 1976

"Recognizing the potential impact that stratospheric pollution and a reduction of the ozone layer may have on mankind

Requests the Executive Director to convene a meeting of appropriate international governmental and non-governmental organizations:

to review all aspects of the Ozone Layer,

identify ongoing activities and future plans, and

agree on a division of labour and a coordinating mechanism for : inter alia,

the compilation of reserach activities and future plans; and
the collection of related and commercial information".

This paper, for presentation at the UNEP Ozone Meeting in Washington, D.C. March 1-9 1977, represents an overview of the natural stratosphere and its impacts on man, the biosphere and climate. It has been prepared as a general review of the subject to provide a background for the more detailed and substantive material to be presented by governments and agencies. It does not deal specifically with research gaps, recommendations and organizational matters. These will emerge from the meeting and be included in the final report. It is based on existing state of the art documentation provided by participating organizations and countries. Major parts of the paper are taken from the material supplied by ICSU-SCOPE. Significant material was obtained from documentation by WMO, FAO, ICAO, OCED and UNESA. Other information was gleaned from supporting documents supplied to UNEP or available in national and international publications.

2. The Problem

The existence of the Earth's ozone layer and its vital importance to life on this planet have been known for many years. It is also known that man evolved and adapted over millions of years, to a particular level of ozone in the atmosphere. But only recently has it been realized, that some of man's activities could lead to stratospheric pollution and to a significant reduction in ozone amounts, in a few decades.

The absorption of solar ultraviolet radiation (UV) by ozone, provides the heat source which maintains the stable stratosphere (the cap to the turbulent weather systems of the troposhere) and is thus one of the ultimate controls on global climate. More importantly, this absorption process shields the earth's surface from most biologically damaging UV (i.e. UV-B)* and increased penetration of this radiation is expected to have detrimental effects on many forms of life.

* UV-B = 290-320nm.

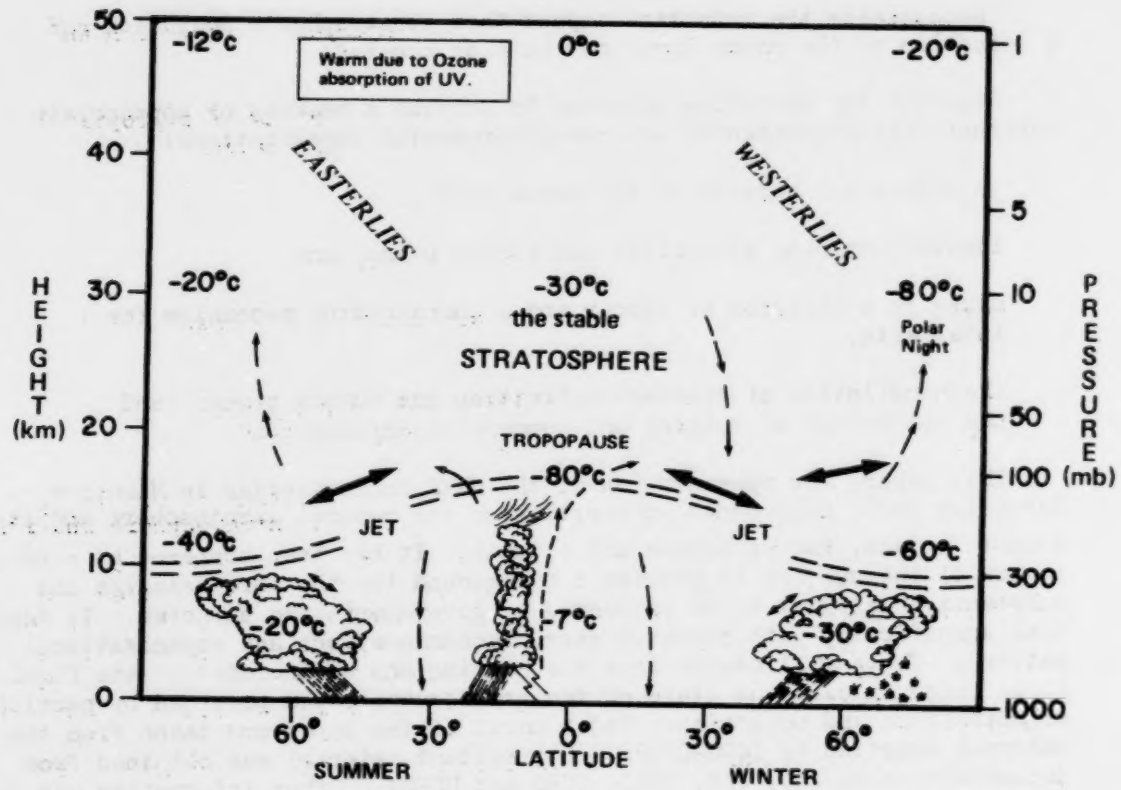

Figure 1 THE NATURAL STRATOSPHERE

The natural stratosphere is warmed from above by the absorption of ultraviolet radiation by Ozone. Hence the temperature increases with height, a temperature inversion, so the stratosphere is strongly stratified and vertical mixing is very slow (order of years). Much of the lower-level water vapour is apparently filtered out by the - 80°C cold trap at the tropical tropopause, hence the stratosphere is virtually cloudless. In contrast the troposphere is heated from below, temperatures decrease with height and vertical overturning is fast (order of days), except in low-level inversions. Most pollutants introduced into the troposphere are subject to rain out and only those that are very stable, such as N_2O, CFMs, etc. reach the stratosphere in significant amounts.

There is thus a great need to understand the physical and chemical processes involved in the ozone layer, the effects of global ozone changes on climate and the effects of increased UV-B on life systems, and to monitor the atmospheric parameters, including radiation, and the active trace gases (primarily nitrogen oxides and chlorofluoromethanes, CFMs) - to provide a sound basis for any necessary action to safeguard this fundamental part of the global environment.

3. The Natural Stratosphere and Ozone Layer

3.1 The Stratosphere

The vertical structure of the atmosphere is largely determined by the way in which incoming solar radiation, interacts with atmospheric constituents (nitrogen-78%, oxygen 21%.....). Above 100 km is found the very high temperature and complex thermosphere, where all constituents are eventually broken down, and where most of the very short wave radiation is absorbed. Between 50 km and 30 km, short wavelength UV breaks down very small amounts of molecular oxygen (O_2) into atomic oxygen (O) and these recombine to form ozone (triatomic oxygen O_3). The resulting concentration of ozone is only about one millionth of that of oxygen. The ozone in turn absorbs most of the solar sunburning UV-B, thereby creating a warm region where temperatures may approach surface values (N 0°C). The bulk of the solar energy, which is in the visible part of the spectrum, passes through the transparent atmosphere, to be absorbed at the surface of the earth where it creates the warmth of the land and oceans.

The region of the atmosphere closest to the surface of the earth is called the troposphere. Away from the solar heating at the surface temperatures normally decrease with height up to the tropopause, the base of the stratosphere.

The tropopause is found near 17 km (temperature/-80°C) over the warm equatorial regions, but only 12-8 km (temperature/-50°C to -60°C) above the temperate and polar regions. Above the tropopause there is normally a temperature inversion, and temperatures increase with height up to the major heating region near 50 km, the top of the stratosphere.

The troposphere is relatively turbulent and well mixed, compared to the stratosphere where the temperature inversion prevails. Moreover the active weather systems and precipitation, in the form of rain and snow, are largely confined to the troposphere. For these reasons most pullutants injected into the troposphere will be removed from the atmosphere through physical processes such as rain-out or contact with the surface within a week. In contrast, a pollutant introduced into the stratosphere can remain there for several years before being transported vertically into another layer. It should be mentioned

that the broad horizontal wind currents in the stratosphere tend to be as strong as they are in the troposphere, hence injected stratospheric pollutants may be widely distributed over the globe in a relatively short time even though their vertical exchange is very slow.

Because the upper stratosphere is heated by the sun's radiation, it must show large seasonal variations following the sun. Hence, temperatures change little near the equator (50km/0°C, 30km/-30°C) but the summer pole is very warm (50km/+12°C, 30km/-20°C) and the winter pole, without sunshine, is very cold (50km/-20°C, 30km/-80°C). The summer hemisphere is then dominated by a warm stable anticyclone, centred on the pole, with winds from the east (easterlies) covering the entire hemisphere. The tops of the tropospheric weather systems are quickly damped by this flow and can scarcely be seen in the wind patterns at 20 km. On the other hand, the winter polar stratospheres feature a cold cyclonic vortex (low pressure area) and west winds extend outwards towards a subtropical high pressure (anticyclonic) belt. The largest scale weather patterns - planetary waves - which are generated in the tropospheric westerlies can propogate to great heights in the stratospheric polar westerlies. Interactions between these two systems, produce large oscillations in the stratospheric polar vortex (which has much less mass than its tropospheric counterpart), at times leading to its breakdown in what are called sudden stratospheric warmings. It is not yet known, to what extent these interactions modify the tropospheric patterns and their long range prediction. As the tropospheric systems vary considerably from the northern to the southern hemisphere, so do the details of the warmings in the two winter statospheres. In between these great monsoonal changes at higher latitudes, the equatorial regions tend to show a superimposed two-year change, from east to west to east winds (quasi-biennial oscillation).

3.2 The Ozone Layer

The small amount of ozone present in the stratosphere, is the result of a balance between processes which form it and others which destroy it. The production processes involve rather fast interactions, between short wavelength UV(250nm) from the sun and normal oxygen in the upper stratosphere. Since neither the strength of the sun's radiation nor the amount of normal oxygen in the atmosphere*can be changed*by human intervention, nothing man does will likely alter the production rate.

The destruction processes of ozone in the natural statosphere were thought to be the recombination of ozone and atomic oxygen and some ultraviolet breakdown. However, it is now a well established fact that nitrogen oxides (NO derived from N_2O) participate in the natural destruction and may account for 70% of it, even though the concentrations of such trace constitu nts are generally only a few parts per billion (i.e. about 1000 times less than ozone itself).

* reference is to changes significant for ozone layer processes

The reason why a small amount of a substance such as nitric oxide, can destroy a much larger amount of ozone is that it reacts catalytically, i.e. one molecule of nitric oxide decomposes about 1000 molecules of ozone, before it itself is removed. (It is the destruction phase) that can be perturbed by man's activities).

Nevertheless the main production and destruction processes in the stratosphere take place on a very short time scale, and in the presence of short wavelength UV. They are very effective, in sunlit regions above 25 km and determine the, more or less, steady amounts of ozone there. Any ozone transported out of this region is quickly replaced. Below 25 km, the effective UV radiation and its by-products rapidly peter out and ozone becomes a quasi - conservative constituent of the atmosphere, until it reaches the ground where it again decomposes. Ozone may thus be said to be produced in the sunlit stratosphere above 25 km, transported to and stored in the middle and lower stratosphere below 25 km, and destroyed at the ground. Average concentrations of ozone increase downwards to about 10 parts per million (10ppm) at 25 km; they may remain relatively high through the lower stratosphere, then drop very rapidly across the tropopause and remain fairly constant, at about .1ppm, through the mixed troposphere to the sink at the ground.

The total amount of ozone overhead* is an important quantity, for it determines the amount of UV-B penetration to the earth's surface. Since the bulk of the ozone (85-90%) lies in the stratosphere, between the tropopause and 30 km, it is the depth of this layer which, first of all, defines the horizontal variations of total ozone, modified to some extent by the vigour of stratospheric transports. Hence the ozone layer is thin, about 250 units* over the equator where the tropopause is at 17 km, and its thickness increases rapidly to about 300 units at mid-latitudes, as the tropopause drops to about 10-12 km. At the middle and high latitudes travelling weather systems also affect the lower stratosphere and the height of the tropopause, so that ozone variations of 100 units over a few days are often observed, being perhaps 400 units behind surface low pressure areas and 300 units behind moving anticyclones. In addition, the vigorous oscillations in the stratospheric winter vortex result in large poleward ozone transports, and accumulations may bring total ozone amounts up to 500 units, in the later winter and early spring, in the north polar regions. In the south polar regions, spring values are somewhat less due to the reduced frequency of the stratospheric warmings. During the quiescent summer period, in the stratospheres of both hemispheres, total ozone amounts gradually subside, generally being slightly less than 300 units, at middle and high latitudes, through the fall months.

Using a global mean of 300 units, total ozone varies: latitudinally by 35%; seasonally by less than 10% at the equator,

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* The average total ozone overhead is equivalent to a column at STP of about .3 cm or 300 Dobson units.

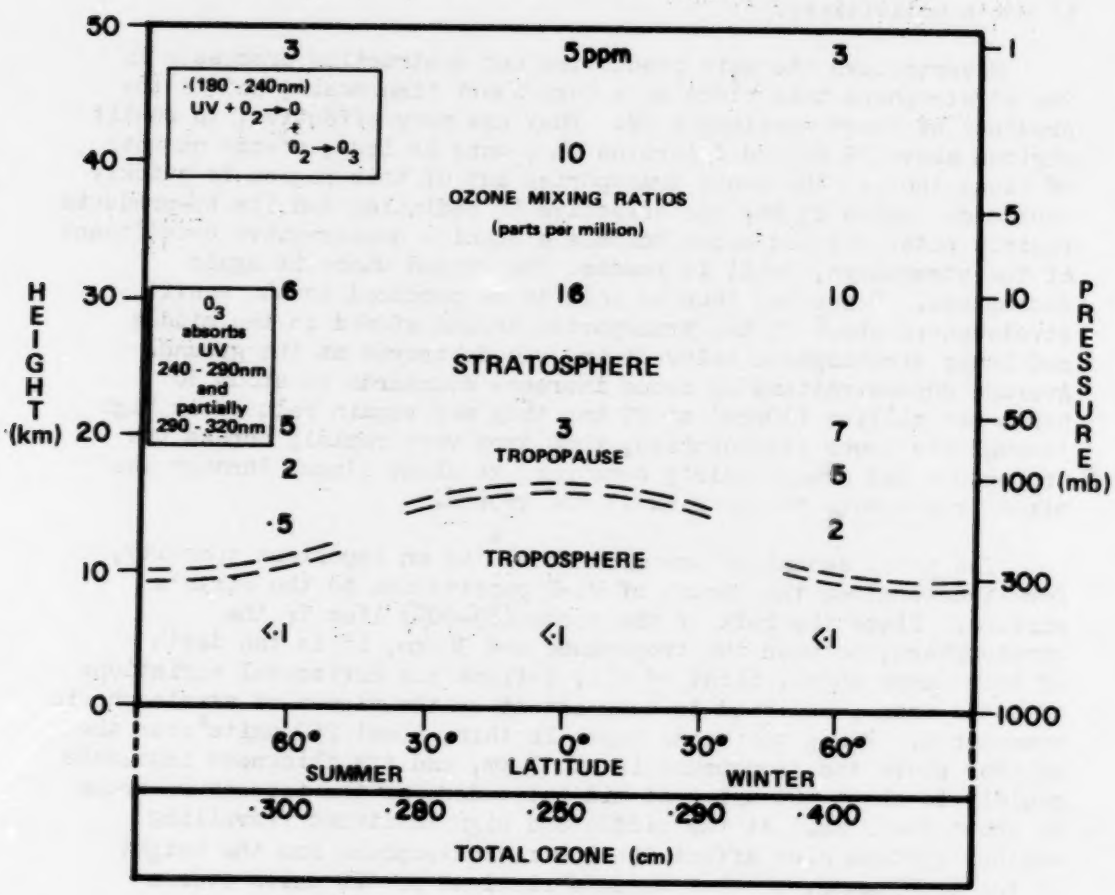

Figure 2 THE OZONE LAYER

Ozone is created by the action of short wavelength ultraviolet radiation (UV), on a very short time scale, at levels above 25 km where it is found in fairly steady concentrations. At lower stratospheric levels it is almost conservative (neither created nor destrpyed) and moves about with the air, so that amounts are quite variable. For motions, the conservative quantity is the mixing ratio which does not change as the air moves up and down. The ozone mixing ratio tends to have a maximum of about 16 ppm above 25 km. However, the contributions to the total ozone column have to be mass-weighted so that the layer from the tropopause to 30 km largely determines the total ozone and its variations. The total ozone amount is thus small in the equatorial regions (.250 cm) and considerable greater at middle and high latitudes (.300 to .500 cm) and varies in space and time roughly as the height of the tropopause varies.

about 25% at high southern latitudes and 50% at high northern latitudes; over short periods (days) up to 35%; and over longer periods in the 10-20 years of records (After removal of the annual oscillation) variations from the mean , at single stations, are generally within ± 5%, and averaged over the globe within ± 2% It would thus appear that a shift in the global mean, of 2% in 20 years, might be difficult to interpret, but that a 5% shift in 20 years would stand out clearly from natural variations.

4. Ozone and Related Measurements

Most atmospheric constituents can be sensed, either through their absorption at solar wavelengths (e.g. O_3, NO_2, CH_4, N_2O, ClO). or by their emission at terrestrial wavelengths (e.g. temperature/CO_2, O_3, H_2O, HNO_3 OH, N_2O, N_2O_5). Others are susceptible to in situ measurements, by electro-chemical and similar techniques (e.g. H_2O, O_3, NO). Still others, because of very low concentrations etc., require the taking of air samples and subsequent laboratory analysis by techniques such as gas chromotography (e.g. F11, F12, CCl_4).

The Dobson ozone spectrophotometer measures the relative intensity of transmitted sunlight, at two different wavelengths in the UV, one being strongly and other only weakly absorbed by ozone, to determine the total amount of ozone overhead. Observations on the zenith sky, as the sun rises or sets through the various atmospheric layers, yield a crude vertical ozone profile, via the umkehr (inversion) technique. Measurements of total ozone, at most of the 80 station WMO network, are made with Dobsons, although some stations use a somewhat less stable filter instrument. With careful handling, maintenance and regular recalibration against a reference standard, the Dobson has an accuracy of about 2%. Individual inaccuracies across the network may be up to 10%. A new grating spectrophotometer, with modern digital electronics, has been developed in Canada and a new filter instrument in New Zealand. Both need to be tested operationally against standard Dobsons.

The vertical ozone distribution is measured in situ, at about a dozen stations using radiosonde attachments, and at a few rocket stations. These are normally calibrated against local Dobson total ozone observations. Intercomparisons of the various electro-chemical and other types of sondes are necessary.

Satellite measurements of total ozone and its upper level distribution are made using ultraviolet back-scattered from the ozone layer (B-UV data), by limb-scanning techniques and by radiometer scanning of the infra-red emissions. Their absolute accuracy and distributions below 25 km are somewhat low, but they can be calibrated against the ground-truth Dobsons and ozone sondes, and the accuracy should improved steadily. They provide a wealth of detail on the global distributions, relationship to weather system and geography, and are almost essential to the study of special events. Future trends will be much easier to identify with satellite data.

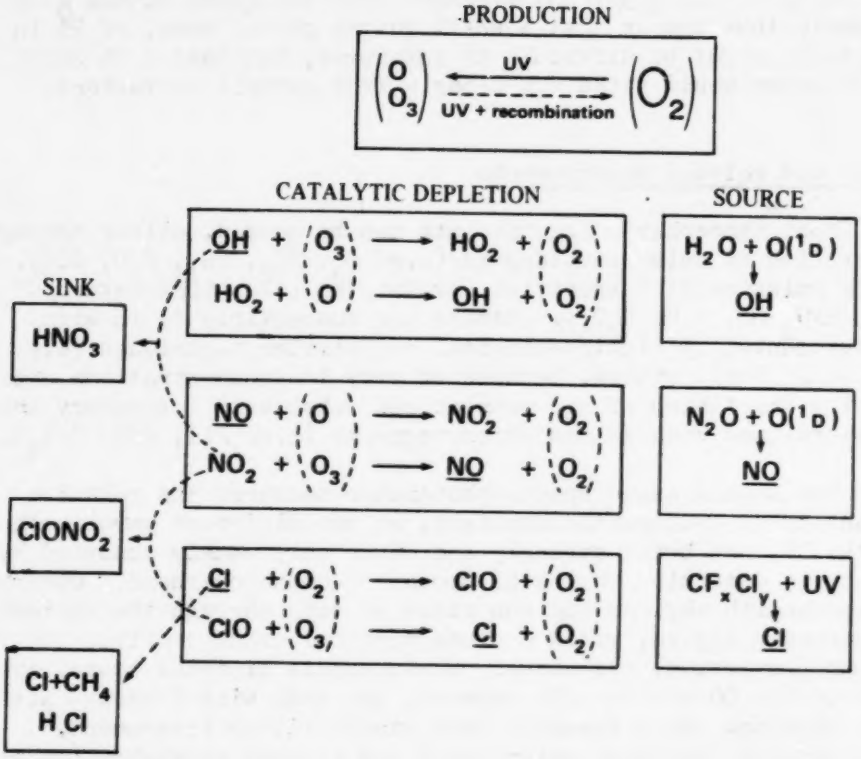

Figure 3 SIMPLIFIED OZONE PHOTOCHEMISTRY

The stratospheric production and destruction of ozone occur mainly above 25 km where short wavelength ultraviolet radiation is available for photolysis. On the production side the photolysis of molecular oxygen, O_2 creates atomic oxygen, O which recombines with O_2 to form ozone, O_3. In the absence of catalytic substances, the ozone production would be balanced partially by photolysis and partially by recombination. The three main catalytic cycles thought to be active in the atmosphere are shown below the production cycle. The most important one in the natural stratosphere is the nitrogen system, the source being nitrous oxide and the sink nitric acid. It is now thought to account for about 70% of the high-level ozone destruction. The chlorine cycle may become significant through the man-made CFM sources.

Note that all three systems interact and that this is a highly simplified version of a complex process.

Atmospheric measurements of trace constitutents are very difficult, as often amounts are only in parts per billion. However, considerable efforts have been made, in a number of countries, using aircraft and skyhook type ballon platforms. These will be enhanced by planned satellite and space shuttle experiments. Many of the active trace species in the hydrogen - nitrogen - chlorine systems have been measured, and new data are appearing regularly. Much further work needs to be carried out, as this is only practical way to verify the laboratory and model schemes for predicting ozone depletion, on a reasonable time scale.

5. Photochemistry and Minor Constituents

5.1 The Role of Minor Constituents

The distribution of ozone in the atmosphere, as has been shown, is governed by photochemistry and atmospheric transport in the stratosphere. The basic photochemistry is set by the photolysis and recombination of oxygen species, which is modulated by the catalytic action of trace substances, primarily found in the hydrogen, nitrogen and chlorine systems. To be effective, these trace substances must be products of compounds which diffuse upwards from the surface of the earth and which are stable enough to survive breakdown and rainout in the troposphere; or must be injected directly into the stratosphere; or must be created there. In order to understand and predict these processes, the full chemical reactions schemes must be determined by laboratory procedures; the processes must be simulated by complex numerical models, which include atmospheric transports; and finally the distributions of the trace constituents must be measured in the atmosphere, to verify and modulate the first two. Fortunately, advanced work has been carried out in a number of countries. Complex one and two dimensional models, with oxygen-hydrogen-nitrogen and chlorine chemistry, can now simulate the natural distributions quite accurately, and reasonable confidence can be placed in their ability to predict the effect of modifications.

5.2 The Hydrogen System

The catalytic agent is the hydroxyl radical, OH, which is formed by the fractionation of water or methane CH_4, in reaction with electronically excited oxygen, $O(^1D)$. Methane is produced by bacterial action in marsh lands and lakes. In the natural stratosphere these reactions increase the destruction rates by less than 10%. A doubling of the stratospheric water content, in atmospheric models, yields less than 1% change in total ozone, so its modulation by man is unlikely to be significant.

5.3 The Nitrogen System

The catalytic agent is nitric oxide, NO. In the natural stratosphere the source is primarily nitrous oxide, N_2O, which is produced by denitrifaction processes in the soils

and oceans. After diffusion into the stratosphere, N_2O reacts with excited oxygen to form NO. The catalytic cycle is interrupted by interaction with a hydroxyl radical to form nitric acid which diffuses downwards into the troposphere and is rained out. This process accounts for up to 70% of the destruction side of the ozone process - in its absence, natural ozone amounts would be much higher (1.5 to 2 times).

At high temperatures, molecular nitrogen and oxygen, the major constituents of the atmosphere, combine to form nitric oxide, which is thus produced in combustion processes and nuclear explosions. Other NO sources are lightning, galactic cosmic rays and solar proton events. Only the NO produced in the stratosphere is effective in destroying ozone there.

5.3.1 Fertilizers

The application of nitrogen fertilizer over the globe is currently about 50 megatons per year and may increase to 100-200 MT/yr by the year 2000. In all other processes the nitrogen fixation is about 200 MT/yr. Fertilizer use would thus be expected to have some effect on the denitrification process, which produces molecular nitrogen, N_2 and a small amount (~7%) of nitrous oxide, N_2O. It is the latter which eventually reaches the stratosphere and accounts for a large part of the ozone destruction. The process of denitrification, in the soil and the sea is not well understood. In particular, there may be a very long time lag between fertilizer application and denitrification. Denitrification may also be affected by the acidity of the soil, another pollution problem.

Estimates of the fertilizer effect on ozone destruction, range from pratically nil to as high as 15% by the end of next century. Much further research on the nitrogen cycle is needed, before any confidence can be placed in these figures.

5.3.2 Aircraft

The advent of the supersonic aircraft, whose high temperature combustion engines inject nitric oxide directly into the stratosphere, provided the spur for major research programmes on the perturbed stratosphere. These definitive studies show that the ozone reduction is related to the injection rate, and to the injection altitude (closeness to ozone production zone). Hence subsonic aircraft injections in the troposphere are not expected to have a noticeable effect, nor are small numbers of concorde-type aircraft operating at 17 km or lower. On the other hand, models indicate that a fleet of advanced SSTs, operating at 21 km with an injection rate of 1.8 MT/yr, could result in a 12% steady state ozone depletion. Continuing studies will be required to monitor current emissions and to determine whether emission controls would be required if such fleets come off the drawing board.

5.3.3 Nuclear Explosions

Nitric oxide produced by the high temperatures is a nuclear explosion should result in ozone depletion. Some ozone may be created locally by UV radiation from the fireball, but after a few days, this effect should die out and depletion from nitric oxide grow in importance. The magnitude of the depletion effect again depends critically on the injection level, and on subsequent stmospheric diffusion and transport of the nitric oxide. So far intensive studies using total ozo e, ozone sondes and, more recently, satellite measurements have failed to reveal any noticeable effect subsequent to nuclear explosions. On track measurements of ozone and nitrogen oxides may help to resolve the apparent discrepancy between theory and observation.

5.3.4 Galactic Cosmic Rays and Solar Proton Events

Cosmic rays cause ionization and the production of nitric oxide, mainly in the polar lower stratosphere. Suggestions that periodic variations in this production rate might explain some ozone data variations, have not been supported by model simulations. Variations of NO production, equivalent to that suggested for maximum to minimum, produce a small percentage change in polar stratospheric mixing ratios, but no noticeable model variations in total ozone.

Energetic solar particles, entering the atmosphere at high geomagnetic latitudes, produce nitric oxide, mainly at levels above 30 km. The strong solar proton event of August 1972, produced a significant perturbation in stratospheric chemistry, and further studies of major events should cast light on high level processes.

Large amounts of nitric oxide are also produced, above 100km, by UV action in auroral activity. It is unlikely that this affects the stratospheric ozone budget.

5.4 The Chlorine System

The catalytic agent is atomic chlorine, Cl, which is released when stable chlorine compounds are disassociated by short wavelength UV, in the middle and upper stratosphere above 25km. At lower levels, these compounds are shielded from that UV by the ozone. There is a minor ozone destruction in the natural stratosphere due to methyl chloride, CH_3Cl. However the major new source is from the man-made chlorofluoromethanes (CFMs), primarily, F11, $CFCl_3$ and F12, CF_2Cl_2. When free chlorine is released by the action of UV on a CFM molecule at a median altitude of 30km, it goes through many catalytic cycles in which ozone is destroyed and moved back to the molecular oxygen reservoir. The cycling is interrupted, to some extent, by interaction with the nitrogen system to form chlorine nitrate, $ClNO_3$, but mostly by interaction with the hydrogen system ($Cl+CH_4$) to give hydrogen chloride, HCl. These compounds diffuse downwards into the troposphere and are eventually rained out.

The time scale for a CFM molecule to reach the 30km level may be as long as 15 years, and its eventual return to the surface, as HCl in rain, about 50 - 100 years.

The CFMs are manufactured from carbon tetrachloride, hydrofluoric acid and chloroform. The annual global production of F11 and F12 rose from .1 million tons in the late fifties to close to 1 million tons in 1974. Since then the production has declined by 10 to 15%, possibly due to economic conditions. About one-half the CFMs are produced in the United States and most of the rest in Europe.

The major uses of CFMs are as propellants in aerosol spray cans, as cooling agents in refrigeration and air conditioning, and as blowing agents in foams. The aerosal sprays account for about 75% of the emissions into the atmosphere, and about 75% of their use is for personal care products - hair sprays, antiperspirants/ deodorants.

A large research effort has gone into verifying the chemical reaction schemes in the laboratory, running these in numerical models of the atmosphere, and measuring the trace constituents and the reactive species in the real atmosphere. The latter measurements are particularly difficult, because of the very low concentrations in the atmosphere and the need to build new precision instruments. Nevertheless, even though there are still significant gaps, much progress has been made. The vertical distribution of the CFMs has been measured a number of times by sampling techniques. They show a constant mixing ratio in the troposphere, and then a decay with height after the sampling balloon has entered the stratosphere - just as the models predict. Measurements of trace constituents, in particular HCl and more recently ClO, have been reported but their distributions are still rather uncertain. The search for alternate chemical reactions, sources and sinks, the many modelling efforts and the atmospheric measurements, albeit still very preliminary, have all failed to reveal any major flaw in the theory. Since it would require at least 15 to 20 years of additional ozone data to sort out an expected atmospheric depletion trend, one must follow the path of chemical and atmospheric prediction systems verified by an atmospheric measurement effort, especially simultaneous measurements of important trace species.

At the present time all reported atmospheric models, including ones by government, universities and industry, yield ozone depletion predictions which fall within the 2 to 20% range at steady state, with a median value of about 8%. These have the following approximate modelling time scales for ozone depletion.* Taking the upper limit case of final depletion at 20% for emissions constant at 1973 level, the models indicate 2% depletion would be reached in 3 years, 5% in 15 years, 10% in 30-40 years and 20% in 100-200 years; a drop in emissions by one-half over the next decade changes these to 2% in 3 years, 5% in 30 years, and 11% at steady state. For the median case of final ozone depletion at 8%, the constant 1973 emission case

* See also figure 4 page 24

figures are 2% in 17 years, 5% in 70 years and 10% never; a drop to one-half over the next decade, changes these to 2% in 32 years and 5% never. Whether one assumes the drop to take place rapidly, or over a decade, makes a difference of no more than 1% or 5 years in the overall figures. For planning purposes one may work with these figures, updated as required by new research results, and turn to the important question of assessing the environmental impact of such ozone reductions.

6. Impact of Climate and Weather

Man's sensitivity to the vagaries of climate and weather is ever present in the tragedies of cold regimes, drought and flood. Even small changes is global temperature values may have large consequences - a change of only one degree made the difference between the Little Ice Age and the current climate which has nutured advanced technologioal and agricultural developments. Even though the models predict sizeable temperature changes in the stratosphere associated with ozone reductions, the predicted temperature changes at the earth's surface are scarcely separable from the model noise.

However, there are still two aspects of the climate problem that require further consideration. It is well known that very small shifts, in the atmospheric planetary waves and large scale circulation patterns, can result in dramatic changes in temperature and precipitation regimes. These planetary waves are neither well understood, nor well predicted in atmospheric models. It is suspected that their vertical structure may be important; hence until the problem is resolved, one cannot rule out the possibility of changes, in the ozone layer and stratospheric temperature, having an impact on weather patterns.

Of more importance, in this context, may be the fact that the CFMs absorb atmospheric radiation strongly in wavelengths where other absorptions are weak (in the atmospheric radiation window). Hence radiation, that would normally escape to space, is trapped by the CFMs in the atmosphere, just as other wavelengths are trapped by carbon dioxide and water vapour - keeping the earth warm by the greenhouse effect. Continued CFM release at the 1973 rates yields a contribution to the global temperature trend of about plus 0.5°C at steady state - about one sixth the predicted effect of increasing carbon dioxide concentrations. These are part of the general climate problem and, since they are as large as observed natural variations on the time scale of a hundred years, they need serious research consideration. (In the words of WMO - it is not yet possible to predict even naturally induced climate changes, for the next year, decade or century, with any useful degree of confidence.)

7. Impact of Increased Ultraviolet Radiation

7.1 The UV Spectrum

Ultraviolet light is invisible and each of its phtons is of shorter wavelength and more energetic than visible light which has a range from 400 to 750 nm.

UV shorter than 180nm does not reach the stratosphere; from 180-240nm it is absorbed primarily by O_2 to make O_3 and deos not reach the lower stratosphere; from 240-290nm it is absorbed by O_3 and does not reach the earth's surface; from 290-320nm (UV-B) the radiation is partially absorbed by Ozone and the portion which does reach the earth's surface is largely responsible for sunburn, skin cancer and other biological effects, and from 320-400nm (UV-A) the radiation is mostly transmitted to the ground and may be important in the formation of phto-chemical smog.

Even though the shorter the UV wavelength the greater the biological effect the transmitted UV-B is effectively terminated at 290nm since shorter wavelengths do not reach the ground. The relative effectiveness (or the action spectrum) of UV-B in altering DNA, the material carrying the genetic information of all living cells, increases by a factor of about 15,000 as wavelengths drop from 320 to 290nm*. It follows that wavelengths in the middle of the band (~305nm)contribute most to biological effects. Under clear skies the transmission at the middle of the band is about 30% for 250 units of total ozone (tropical values) and less than 10% for an extreme value of 500 units of ozone. The biological effect integrated over the spectum is found to vary about twice as fast as the total ozone variation - i.e. a decrease in total ozone of 10% would result in an increase of about 20% in the weighted sum of the UV-B - (henceforth simply called SUV-B).

If one sets the SUV-B at 10 arbitrary units at the equator, then the annual average is about 4 units in middle latitudes. In winter it varies from 10 to 1, and in summer from 10 to 6 units, from equator to mid-latitudes. These values are in general agreement with SUV-B measurements at the ground. It should be noted that, although long term exposure values are much lower at middle and high latitudes than at tropical latitudes, the main summer growing and exposure seasons at higher latitudes receive only fractionally lower amounts than the tropics.

One latitudinally dependent model gives a somewhat greater ozone depletion in the summer hemisphere for nitrogen (NO) perturbations, and in the winter hemisphere for chlorine (CFM) perturbations. These are probably within error limits; hence

* This variation defines the action spectrum of UV-B for DNA, deoxyribonucleic acid.

a given percentage ozone depletion may as well be considered the same at all latitudes.

Thus the major errors will not lie in estimations of the change in transmitted UV-B for a given change in total ozone, but rather in the assessment of the damaging effect on living organisms, or their action spectrum. Whilst the action spectrum for unrepaired damage to DNA gives a useful approximation, the real effects can only be assessed from a knowledge of the wavelength to damage response, in each case. In general these action spectra are complicated by screening and photo-repair mechanisms and by photosensitization effects. They are rather poorly known, if at all, and require much further research and documentation.

7.2 The Photobiology of Damage by UV

There is a wide range of deleterious effects from solar UV, including the well-known bactericidal and erythemal (skinburn) actions. Unfortunately, most of the basic photobiological research has used low-pressure mercury lamps with most of the emission at 254 nm, which is close to the absorbance peak for DNA and RNA,* but is not present in the solar spectrum reaching the ground. Extrapolations from results at 254 nm to the 290 - 320 nm UV-B are not straight-forward. The research has concentrated on effects of UV absorbed by proteins and nucleic acids and has led to a good understanding of the photochemistry and photobiology of DNA damage.

The most common cause of UV damage in DNA is the formation of thymidine dimers, which prevents the separation of the DNA double strands, resulting in cell death in microorganisms, including phytoplankton. Lesions in cells may be repaired by dark recovery or by photoreactivation, involving an enzymatic process. During the important process of photoreactivation, the thymidine dimers formed by UV radiation below 300nm are separated by the action of 300-475nm UV, and thymidine monomers are regenerated. The synthesis of a new component of DNA, from information on the complementary strand, can then be effected.

In single cells, which have unusually effective DNA repair mechanisms, reactions of proteins become of relatively greater importance. UV irradiation of proteins causes a poorly characterized assortment of reactions in their component amino-acids. The repair mechanisms are also not well known.

Higher organisms show the same principal kinds of photochemical damage to nucleic acids and proteins as microorganisms, with similar repair processes. However, the prediction of UV-B effects is complicated by the fact that the net unrepaired damage, unlike the initial damage, may not be proportional to UV exposure.

* DNA — deoxyribonucleic acid; RNA - ribonucleic acid

To assess and predict possible damage one needs to know not only the relative effectiveness of different wavelengths but also dose-response relationships, (i.e. whether low intensities for a long time give similar results to high intensities for a short time, and whether interactions in higher organisms can differ under natural conditions). Simple systems can be studied experimentally by the use of solar simulators, but the effects on man and large ecosystems must be derived from theory or from correlation studies, which are often difficult to interpret.

7.3 Impact on Man

The effects of UV-B exposure on man include sunburn and snow-blindness, as well as eye damage and ageing and wrinkling of the skin. These can be avoided or lessened by suitable protection. The production of vitamin D_3 is generally thought to be beneficial, but excessive intake may possibly cause intoxication.

There is substantial evidence to link UV-B with skin cancer. Sun-induced skin cancers are generally diseases of less pigmented peoples and are probably caused by the action of UV-B on DNA. Work with laboratory animals is consistent with this conclusion. The most common skin cancers (non-melanoma) are only locally invasive and respond to treatment. They occur, most frequently, on habitually exposed areas of the body and show a strong correlation of incidence with latitude. These observations, together with differences linked with occupational exposure, point clearly to sunlight as prime cause of cancer induction, and to increased incidence as a consequence of increase in UV-B. Generally disseminated skin cancer (melanoma) is much rarer but has a very high mortality rate and, therefore, represents a significant health hazard. The evidence linking ultraviolet radiation with melanoma is not so strong as for non-melanoma. The latitude dependence is well established, but melanoma is not concentrated on the habitually exposed areas of the body. However, it is rarely seen in the regions which are least exposed (e.g. those usually covered by a bathing suit), and most cases are found in those areas which are lightly covered or occasionally uncovered. Differences in patterns of location between sexes correlate with differences in exposure to sun, with more on the chest in males and on the legs in females. There is, therefore, still a strong likelihood that solar UV contributes to the induction and/or to the development of melanoma, and that an increase in UV-B reaching the ground would result in an increase in melanoma incidence and mortality. Where UV contributes to the induction of cancers, the dose-response relationships are complex and unknown and quantitative predictions can only be speculative. A decrease in the uncertainty, associated with these predictions, requires not only a better basic understanding of the origin and growth of skin cancers, but also better epidemiological data.

7.4 Impact on Plants

Most of the early experimental work with plants was carried out at 254nm: only relatively recently have possible effects of UV-B received attention. Degradation of chlorophyl , depressed rates of photosynthesis, and cell death, which are among the observed responses to 254 nm UV light, are assumed to be caused by damage to nucleic acids and proteins. Longer wavelengths of UV may also destroy some plant hormones and induce the release of a related substance, ethylene. Experiments with lamp-filter combinations, simulating the increase in UV-B which would be associated with a 35 to 50 percent decrease in ozone, have been carried out in glasshouses, controlled environment rooms and, to a limited extent, in the field. These studies have revealed a great range of sensitivity to damage. Many plants are adapted to grow in full sunlight and mechanisms to cope with potentially damaging UV-B have developed. These include elaboration of effective screening pigment systems in the outer layers which protect the photosynthetic apparatus, temporal separation of UV-sensitive reactions such as cell division so that they occur mainly during darkness, repair systems, and possibly some degree of avoidance by positional movements. It was found that some plants tolerated an increase in UV-B, such as might accompany a 50 percent depletion of ozone, while others showed signs of stress with regimes that are considered normal fluxes of UV-B. In sensitive species, the increased UV inhibited growth and development, depressed photosynthesis and biomass, and enhanced somatic mutation rate. Pollen germination was also found to be inhibited. Depressions in growth rate and biomass have been documented in the field for some species in Utah, and in glasshouses with the roof removed in Florida. However, there is a great heterogeneity of response, depending on species and environmental conditions; and a greater degree of damage is observed, more commonly and to an enhanced degree, under growth room conditions than in the field. This is possibly because of the greater amount of light available for photo-repair under the latter conditions. The importance of photorepair for plants growing in the open has been demonstrated for some alpine plants, where one day of exposure to normal levels of solar UV without visible light resulted in photochemical damage. It is possible that some higher plants may be able to adapt to a gradual increase in UV-B e.g. by increased pigmentation, alteration of surface wax layers, etc.

In most experiments solar UV has been supplemented to correspond roughly to a 35 to 50 per cent reduction in ozone at 60° solar altitude; the effects of exposing sensitive plants to lesser degrees of ozone depletion have not yet been well explored. The dose-response relationships have not been well investigated but certain types of damage, such as the depression of photosynthesis, appeared to be cumulative. Other types of damage, for example, in inhibition of leaf expansion, seemed to be more affected by peak dose. In general, exposing plants to UV-B causes damage similar to that found in the shorter wavelength region. Photosynthesis, in particular, appears to be sensitive to UV irradiation, which results in ultra-structural changes in the chloroplasts and an overall loss of photosynthetic capacity.

7.5 Impact on Terrestrial Animals

The effects of UV-B radiation on animals other than man have generally received little attention, as it is assumed that they are protected by their outer coverings. A few experiments have shown that large doses of UV-B given during the development stage could lead to abnormalities.

In latitudes where long periods of high natural solar UV are prevalent, three effects attributable to UV have been noted in farm animals. These are cancer eye, a form of ocular carcinoma of cattle; pink-eye, a bacterial infection of cattle which is aggravated by UV; and photosensitization, a complex reaction which results in hypersensitivity following ingestion of certain sensitizing agents (often found in plants) together with UV exposure. Carcinomas are also found in goats, sheep and horses, and in most cases they are found in parts of the body lacking protective melanin, such as eyelids and genitals. Most animals will not expose themselves to full sunlight unless they have a way of preventing excessive light from reaching sensitive areas (.eg. by the presence of UV absorbing pigments).

Although UV-B is within the visible spectrum of many insects and might affect their behaviour, it is not yet possible to assess the relative importance of the UV-B component compared with other factors. Preliminary experiments, with simulated increases in UV-B, have so far revealed no adverse effects on pollination behaviour, in which UV-dependent perception (mostly UV-A) of flower markings (honey guides) is often important. Little information is available on growth and development responses to UV; to date only the larvae of a few insect species have been found to be sensitive to prolonged irradiation with large UV doses.

7.6 Impact on Ecosystems

A broader view of the possible biological impact of increased UV-B includes the non-agricultural aquatic and terrestrial ecosystems, which are important to man for timber, recreation, pest and predator balance, and as a food resource. Experiments with simulated solar sources have revealed considerable difference in sensitivity to UV between species; additional UV might therefore influence the ability of some species to compete in a particular natural ecosystem. Changes in plant metabolities could affect the animals that feed on them.

Aquatic ecosystems might also be affected because solar UV has been shown to penetrate to considerable depths in clear waters, and because some plants crucial to the food chain (phytoplankton) are found close to or on the surface of water, as well as the eggs and larvae of some aquatic animal species. The attenuation of UV-B largely depends on the amount of organic matter present: 10 percent of the UV penetrated to a depth of 23m in clear waters of the west equatorial Pacific but only to 20 cm in Douglas Lake, Michigan.

Calculations indicated that about 2 percent of the euphotic zone (the zone with sufficient light for net photosynthesis) might be affected by UV-B with a stratospheric ozone reduction of 25 percent, resulting in 3 to 10 percent of the phytoplankton of the world's oceans receiving more UV-B than is now received at the surface. Preliminary experiments indicate that phytoplankton may be quite sensitive to UV and consequences to the aquatic food chain might, therefore, be far-reaching.

The prediction of effects in large and complicated ecosystems requires knowledge of the penetration of UV into the canopies, the the sensitivity and behaviour patterns of the component species and the species interactions. At present, both the basic data and the models, that would permit reasonably confident predictions for complex natural ecosystems, are lacking.

7.7 The Reduction of Harmful Effects

Some of the radiation effects could be mitigated through educational programmes on the risks involved in excessive exposure to sunlight, and through a conscious effort to breed crops with increased UV resistance. Because predicted solar UV increases take place gradually over decades, selective screening for the increased UV stress would be a natural part of crop development programmes. Long-lived crops, such as trees, would be at a greater risk from the cumulative effects of UV-B exposure.

In natural ecosystems the impact of increased UV-B can only be minimized internally. Some organisms have spare capacity through repair, screening and avoidance mechanisms; others are already near their tolerance levels. Since the behavioural cue for UV-B avoidance is the intensity of visible light, which does not change appreciable with ozone changes, the effectiveness of this cue may be very low.

The UV-B sensitive species of green plants are likely to be the most vulnerable organisms in terrestrial ecosystems because they cannot readily avoid exposure. Long-lived species of forest canopies and grassland plants are likely to be the most subject to cumulative exposure effects.

In aquatic environments, particularly in the open oceans, the avoidance by an increase in depth may not be taken, due to the lack of the visible cue. In some aquatic plants such as phytoplankton, the movement to greater depth may also be associated with greater attenuation of visible light and reduced photosynthesis.

7.8 Summary

Research to date indicates that likely consequences of increased UV-B are: (1) an increase in the incidence of skin cancers with a probable increase in mortality; (2) an increase in carcinoma and perhaps in other UV-B related conditions in cattle, leading to some economic loss; (3) a reduction in crop

and timber yields, which could have social and economic consequences, and (4) a decrease in plankton production with consequences for the aquatic food chain. There might also be changes in the competitive ability among organisms which could alter entire ecosystems, although at present these are impossible to predict. A possible benefit of increased UV-B is the increased production of Vitamin D, although one author concludes that "any hope that an increase in UV might be beneficial should be tempered with caution."

At present, biologists and epidemiologists are being asked to make quantitative predictions from insufficent data. The only predictions that have so far been made are those for the increase in incidence of certain types of skin cancer. The nature of the inherent problems has been stressed : the main targets for UV damage are the important biological macromolecules, proteins and nucleic acids, although in plants destruction of other molecules (e.g. the plant hormones) may add to the damaging effect and be a cause of depressed growth rates. However, extrapolation from laboratory data, obtained with single-celled organisms or cell cultures, to multi-cellular organisms under natural conditions is immensely complicated by screening effects of the outer layers, by behavioural characteristics, by antagonistic and synergistic effects between UV-B light and other wavelengths, and by the presence of repair mechanisms of varying degrees of effectiveness. Experiments with UV-B have now begun in many places, but a realistic evaluation of the possible damage to man and the biosphere, that might arise as a consequence of ozone depletion to any particular level, requires the input of new information, a refining of the models for predicting damage to individuals and to ecosystems, and a programme of long-term research.

8. Summary of findings on Ozone Depletion and its Impact on Man and the Biosphere

1. The total amount of ozone in the natural stratosphere is strongly modulated by nitrogen oxides (emanating from the surface as N_2O), being 1.5 to 2 times less than it might be in a pure oxygen/nitrogen atmosphere.

2. The perturbation of the ozone layer by aircraft emissions of nitrogen oxides is probably negligible at the present time, but could be a matter of concern for future fleets of higher flying, advanced (mach 3) Super Sonic Transports.

3. The perturbation of the ozone layer by CFM emissions is a matter of concern - best estimates now for long term (100-200 years) ozone depletions based on recent emission levels are:

   Upper limit 20%, median 8%, lower limit 2%, with a half life of 40 to 50 years (time to reach one half the percentage depletion)

4. The ozone perturbations due to nitrogen fertilizers, other halogens and as yet unknown sources cannot be estimated with any

accuracy at this time.

The impact of ozone depletions would be:

1. an effect on climate, although the magnitude is uncertain.

2. an increase in skin cancer, eye-damage, sunburning and skin ageing in man (and some animals).

3. mutagenic and other effects on plants and animals which have limited protective and repair mechanisms.

4. possible changes in ecosystems (effects on phytoplankton etc.), although the magnitude and the dependencies are largely unknown.

On the ozone depletion side recent developments have tended to narrow the uncertainities and increase the general level of confidence in the predictions - conversely, one tends to be more concerned with what is not known than what is known on the impact side.

9. SOCIO-ECONOMIC FACTORS

9.1 Introduction

The ozone layer is a global environmental resource which is vital to life on this planet. It appears to have existed in its current natural state throughout the process of evolution. There have been suggestions that variations due to extreme natural events may have caused the disappearance of some ancient species but these are highly speculative. In light of present knowledge, it is reasonable to assume that the average global ozone amount has been relatively constant but future values may change as a result of man's activities now. That is why the problem falls so naturally within UNEP's 'Outer Limits' programme.

When a potential environmental hazard is identified, it is usual to carry out an environmental assessment prior to formulating any control strategy. Such an assessment should be as quantitative as possible and should involve evaluations of the benefits accruing to society from elimination or reduction of the risk and of the costs inherent in the various ways of achieving such reductions. Quantitative evaluation of the benefits that would result from reducing man-induced risks to the ozone layer is extremely difficult. Not only are the effects indirect and incompletely understood, but also in some cases they are expected to occur several generations after the pollutant emission. Thus the effects are,within the economists' time frame, virtually irreversible in that recovery of the ozone layer to its natural state after cessation of damaging emissions may take as long as a century.

Nonetheless, it is not sufficient simply to identify a threat to a vital component of the environment; there is a further responsibility to press ahead with investigations to elucidate and quantify the effects and thereby facilitate some estimation of the benefits that would flow from reduction of the threat.

In contrast to the benefits, the costs involved in dislocating an industry and in developing alternative technologies and processing and delivery methods, are susceptible to fairly precise calculations.

While the benefits that might result from specific actions to reduce the risk to the ozone layer are not now easily quantifiable and it is not yet possible to justify them on the basis of definitive benefit/cost analyses, the existence of a number of risks to human health and welfare have been identified. One can conclude that the first practical international step is to recommend realistic environmental objectives aimed at setting generally acceptable limits to emissions, which could form the basis for specific control actions as appropriate. In the achievement of such objectives, agencies, nations and industries can utilize fairly precise cost/benefit analyses in the assessment of ways, means and alternatives. It is within these limitations that the following very general qualitative assessments are made.

9.2 The Nitrogen System

The photochemistry and behaviour of the stratospheric nitrogen system have been assessed very thoroughly by the U.S. Climatic Impact Assessment Programme, CIAP, and related programmes in other countries. These programmes demonstrated that the current SSTs do not cause significant (detectable) harm to the ozone layer.

Should the production of advanced SSTs be contemplated it will be necessary to evaluate their potential effects on the ozone layer. Engine emission reductions might prove to be very costly relative to the lower nitrogen oxide emissions of current subsonic fan jets. It should be noted that the SST effects may be large because injection is directly into the ozone layer - for the same reason recovery after any necessary control action would be relatively fast. In any case, thorough cost/benefit studies will have to be carried out by the agencies, nations and industry prior to launching a new endeavour.

Man's increasing demands for energy, food and transportation are responsible for more and more interventions in the natural nitrogen cycle. It is now realized that the whole fluid envelope of the planet, as it relates to man and the biosphere, is tightly bound to this nitrogen cycle, which is itself not well understood. The perturbation of the ozone layer, through the input of additional nitrogen oxides, is only one basis for concern about nitrogen pollution. A cost/benefit analysis of the nitrogen fertilizer impact on the ozone layer probably cannot be made at this time and in any case, it should not be made independently of other nitrogen problems. What can be said is that the results of intensive research programmes to clarify the physio-chemical, biological and socio-economic aspects of human modifications of the nitrogen cycle could be very useful indeed.

9.3 The Chlorine System

Unquestionably, it is concern over the impact of CFMs on the ozone layer that has stimulated current national, international and industrial action in this area. It is thus imperative to have careful analyses of the socio-economic factors to provide a basis for any decision aimed at environmental protection. Such studies have been and are being sponsored by a number of agencies, including UNEP, UNESA, OECD and EPA/USA, and the manufacturing industries. These all stress the lack of quantitative knowledge on the impact side, and hence the impossibility of evaluating benefits.

However, two quantitative approaches are available. The first involves modelling the impacts of alternative scenarios on the ozone layer and the second requires evaluation of the various societal and industrial options.

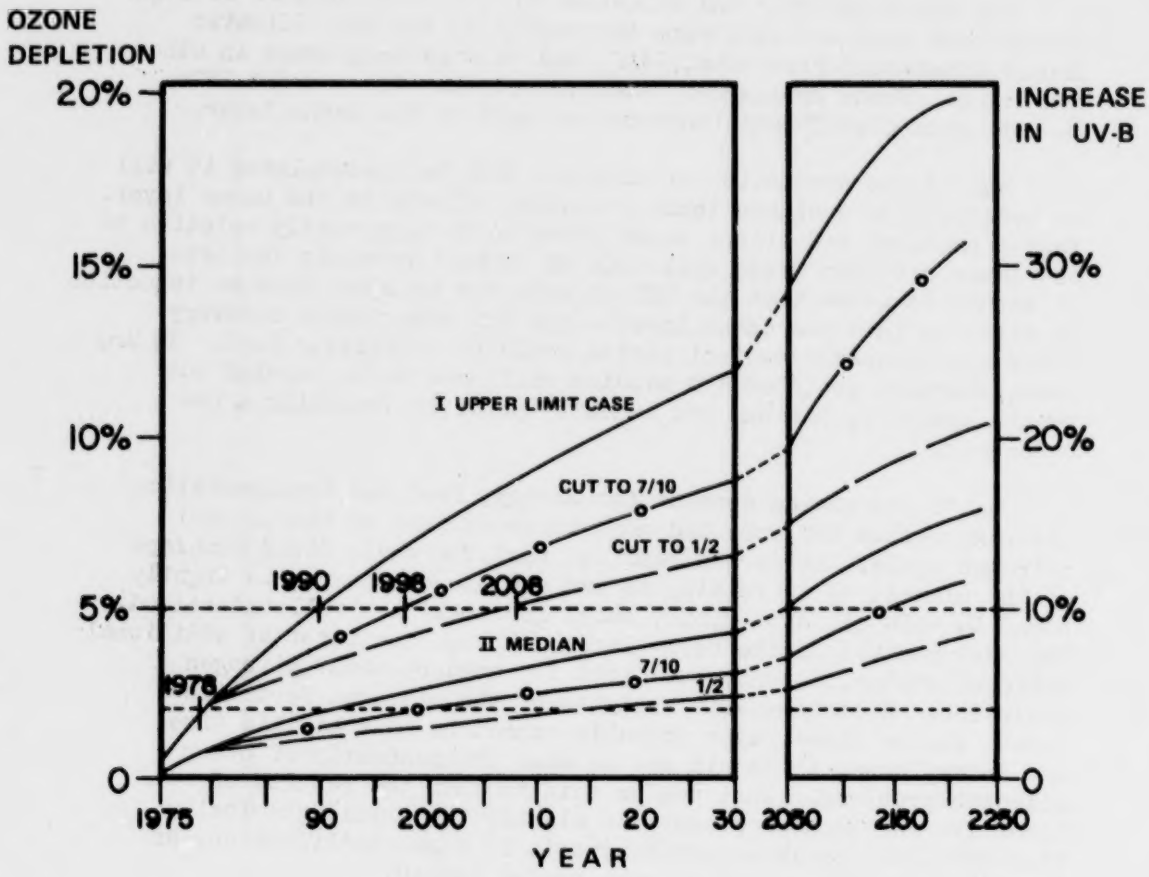

Figure 4 MODEL OZONE DEPLETION

The time scales, for ozone depletions predicted by atmospheric photochemical models under various scenarios, are depicted schematically above. These will vary with the type of model and the assumptions with regard to chemical reactions and diffusion. The diagram is meant to be illustrative rather than definitive. The input in this case is equivalent to constant CFM emissions at the 1973 level. Curve I illustrates the upper limit case of 20% final ozone depletion and curve II the median or 8% final ozone depletion. These are modulated by hypothetical reductions in emission levels in 1978, to seventy percent and then to fifty percent.

The model aspects, which have been reviewed earlier, are calculations which can be easily changed to fit different criteria and easily amended as new research data become available. For instance, if one arbitrarily sets a critical level at 5% ozone depletion (10% increase in UV-B) - then for the upper limit (20% final ozone depletion) case, the critical level for continuing 1973 production is reached in 1990, a drop to 1970 production (to 70%) postpones this date to 1978 and a further drop to 1967 production figures (to 50%) moves this to the year 2008. For the medium (8% final depletion) case, the critical points are respectively 2050, 2150 and never. The significance of such delays lies in the time allowed for more definitive research, which would narrow the uncertainties and clarify the need for either lesser or greater reductions. What they illustrate is that even modest restraints on production or use (and subsequent release) would have a significant impact on future ozone depletions and, presumably, on long-term socio-economic benefits.

Considering the consumer and industrial options, one can make preliminary relative evaluations from data already published. These show that there are three main sectors using CFMs: 1) aerosol propellants 2) refrigeration and airconditioning and 3) foaming agents in plastics. The approximate ratio of their shares of CFM release is 15: 4: 1 and of the respective total economic values 2: 25: 1. The data also indicate that 75% of the aerosol propellants are used in personal care products (hair sprays, antiperspirants, deodorants). Significant reductions in CFM release, with minimum economic loss, can clearly be achieved in the aerosol sector. In addition, the societal factor is, largely a matter of personal convenience and there are already some substitutes and alternative delivery systems on the market. Reductions in the refrigeration/air conditioning sector would impact seriously on that industry and the food industry and from a socio-economic viewpoint would be highly undesirable, if not unacceptable. Fortunately, a large fraction of their CFM emissions could be eliminated by better servicing and recovery systems. In the case of foam manufacture from polyurethane and polystyrene, the substitutes for CFMs probably would lead to a substantial loss in efficiency, but better manufacturing control procedures could cut emissions. It follows from these cost/ benefit considerations and on the prudent assumption of the validity of current prediction models, that to continue to reap the great societal benefits from CFM use in medico-pharmaceutical aerosols, refrigeration/airconditioning and some foaming products, society may have to limit its use of those non-essential aerosol sprays containing CFM propellants.* This course of action, along with better industrial control procedures and the wider use of alternatives, may even permit modest growth in essential areas. Once again it has to be stressed that the assessments are still quite imprecise and that major benefits are to be expected from the acceleration of monitoring and research programmes on all fronts.

* more specifically those CFMs such as F11 and F12, lacking hydrogen

9.4 Future Needs:

In order to elucidate the socio-economic factors including both the benefit and cost sides of this problem there is a need to:

- accelerate monitoring and research on all physio-chemical aspects of the stratospheric ozone layer;
- monitor world-wide production and emission of substances, identified as potential modifiers of stratospheric ozone;
- encourage research on climatic impact;
- promote research and investigative studies on the impacts of increased UV-B on man and the biosphere;
- support broader studies of the socio-economic aspects; and
- move forward on the organizational aspects of coordinating these activities and on the general problem of global environmental protection.